Attachment B

Method Specific Data Validation Guidance for Organic Data Validation

Method Specific Modifications Included:

Method 537 Data Validation Guidelines B-1

TO-15 Data Validation Guidelines B-5

<table>
<tr><th>Issue</th><th>Description</th><th>DV Approach and Qualifier Actions</th></tr>
<tr><td>Preservation & Holding times</td><td>The objective is to determine the validity of the analytical results based on the sample condition and the holding time of the sample.</td><td>
<table>
<tr><th>Condition</th><th>Positive Results</th><th>Non-Detects</th></tr>
<tr><td>Sample not preserved with Trizma</td><td>J-</td><td>R</td></tr>
<tr><td>Sample documented as preserved but no record of verification of pH and/or residual chlorine by lab</td><td>No qualification *</td><td>No qualification *</td></tr>
<tr><td>Sample documented as preserved but pH>=8, pH<=6, or residual chlorine present</td><td>J-**</td><td>UJ **</td></tr>
<tr><td>Sample preserved and prepared within the 14-day holding time for extraction and 28 day holding time for analysis</td><td>No qualification</td><td>No qualification</td></tr>
<tr><td>Sample preserved and prepared outside the 14-day holding time or outside 28 day holding time for analysis</td><td>J-</td><td>R</td></tr>
<tr><td>Sample documented as preserved but pH ≥ 9</td><td>J- ***</td><td>R ***</td></tr>
</table>
Suggested notes:
* Sample documentation indicates sample was preserved however laboratory failed to provide documentation of [pH check and/or residual chlorine] verification.
** Sample marked as preserved but reported by laboratory outside optimum range of pH 6 - 8.
*** Sample marked as preserved but reported by laboratory outside valid pH range.
</td></tr>
<tr><td>Initial Calibration</td><td>To demonstrate adequate capability to quantify accurately branched and linear isomers.</td><td>For PFOS and PFHxS, Verify multiple peaks included in the quantitation of each. If peaks are excluded or other information suggests the method was not followed include the statement "The laboratory did not provide sufficient data to determine if branched chain isomers of PFOS/PFHxS were included in the reporting of this analyte in field samples. No data were qualified based on this finding."

For PFOA No quantitative standard exists. If no demonstration of analysis of mixed standard but multiple peaks are included, include the following statement: "The laboratory did not provide sufficient data to determine if branched chain isomers of PFOA were included in the reporting of this analyte in field samples. No data were qualified based on this finding."</td></tr>
<tr><td>Continuing Calibration</td><td>To demonstrate accuracy of calibration</td><td>Within 70-130% of the true value for all but the lowest level calibration.
Within 50-150% of the true value in the lowest level calibration standard</td></tr>
</table>

<table>
<tr><th>Issue</th><th>Description</th><th>DV Approach and Qualifier Actions</th></tr>
<tr><td>Blank Contamination</td><td>PFCs are known to be subject to extreme blank contamination issues from ubiquitous sources. Method 537 introduces special blanks (Field Reagent Blanks and Lab Reagent Blanks) specifically to better identify and act on suspected contamination.</td><td>For all blanks including Field Reagent and Laboratory Blanks
<table>
<tr><th>Where the Blank is …</th><th>And the Sample Result for that analyte is..</th><th>The Action would be…</th></tr>
<tr><td>ND</td><td>Positive /ND</td><td>No Action</td></tr>
<tr><td rowspan="2">< =1/3* MRL (>MDL)</td><td>Positive</td><td>Qualify positive results B</td></tr>
<tr><td>ND</td><td>No Action</td></tr>
<tr><td rowspan="3">> 1/3 * MRL</td><td>Positive AND >10x blank</td><td>No Action</td></tr>
<tr><td>Positive AND <10x blank</td><td>Qualify positive results as unusable (R)</td></tr>
<tr><td>ND</td><td>No Action</td></tr>
<tr><td>Gross or indeterminate and erratic contamination</td><td>Positive</td><td>Professional judgment up to and including Rejection (R)</td></tr>
</table></td></tr>
<tr><td>Surrogates</td><td>To demonstrate consistent quantitation of target compounds through use of surrogate</td><td>
<table>
<tr><th rowspan="2">Criteria</th><th colspan="2">Action</th></tr>
<tr><th>Detect</th><th>Non-detect</th></tr>
<tr><td>%R < 10%</td><td>J-</td><td>R</td></tr>
<tr><td>10% ≤ %R < Lower Acceptance Limit</td><td>J-</td><td>UJ</td></tr>
<tr><td>Lower Acceptance limit ≤ %R ≤ Upper Acceptance Limit</td><td>No qualification</td><td>No qualification</td></tr>
<tr><td>%R > Upper Acceptance Limit</td><td>J+</td><td>No qualification</td></tr>
</table></td></tr>
<tr><td>Internal Standard</td><td>To demonstrate consistent response for comparable quantitation across analysis batches</td><td>Apply IS qualifiers to associated target compounds in impacted samples only.
<table>
<tr><th>Criteria</th><th>Detect Action</th><th>Non-Detect Action</th></tr>
<tr><td>Area response* < 20%</td><td>J</td><td>Professional judgment (Generally R)</td></tr>
<tr><td>20% ≤ Area response* < 70%</td><td>J</td><td>UJ</td></tr>
<tr><td>70% ≤ Area response* ≤ 140%</td><td>No qualification</td><td>No qualification</td></tr>
<tr><td>Area response* > 140%</td><td>J</td><td>No qualification</td></tr>
</table>
*area measured relative to the most recently run CCC</td></tr>
</table>

<table>
<tr><th>Issue</th><th>Description</th><th>DV Approach and Qualifier Actions</th></tr>
<tr><td>MS/MSDs (LFSM/LFSMD)</td><td>To demonstrate whether matrix issues or interferences impact sensitivity and reliable quantitation.</td><td>All actions applied to native spiked sample only.
LFSM/LFSMD Actions % Recovery
<table>
<tr><th rowspan="2">Criteria</th><th colspan="2">Action</th></tr>
<tr><th>Detect</th><th>Non-detect</th></tr>
<tr><td>%R < 10%</td><td>J</td><td>R</td></tr>
<tr><td>10% ≤ %R < Lower Acceptance Limit</td><td>J</td><td>UJ</td></tr>
<tr><td>Within limits</td><td>No qualification</td><td>No qualification</td></tr>
<tr><td>%R > Upper Acceptance Limit</td><td>J</td><td>No qualification</td></tr>
</table>
%R Limits = 70-130% Or 50-150% when spike is <=2x MRL
LFSM/LFSMD Actions RPD
<table>
<tr><th rowspan="2">Criteria</th><th colspan="2">Action</th></tr>
<tr><th>Detect</th><th>Non-detect</th></tr>
<tr><td>RPD < Limit</td><td>No qualification</td><td>No qualification</td></tr>
<tr><td>RPD > Limit</td><td>J</td><td>No qualification</td></tr>
</table>
RPD Limits = 30% Or 50% when spike is <=2x MRL</td></tr>
</table>

Note: Instrument Performance Checks including no verification of peak symmetry are not performed on validation as the information is typically not available.

Method Specific Data Validation Guidelines for Method TO-15
(*Compendium of Methods for Toxic Organic Air Pollutants*, second edition, January 1999)

<table>
<tr><th>Issue</th><th>Description</th><th>DV Approach and Qualifier Actions</th></tr>
<tr><td>Canister certification</td><td>Demonstrates cleanliness of sampling vessel prior to sample collection</td><td>If no canister certifications, all data are unusable and qualified “R”.

Reporting limits of certification must be equivalent or lower than sample analysis reporting limits.

Results for all target analytes must be less than 0.2 ppbv. If this criterion is not met, professional judgment may be exercised. Validator may qualify the affected target analyte in the sample “J+” as estimated high due to possible contribution from contamination, or “R” as unusable.</td></tr>
<tr><td>Canister pressure / leak test</td><td>Demonstrates sample vessel integrity</td><td>Every canister must have documented leak test: Hold 30 mmHg, with less than 2 psig loss over 24-hour period.

If this criterion is not met or not documented, sample data for this canister is unusable and qualified “R”.</td></tr>
<tr><td>Sample receipt</td><td>Demonstrates sample integrity after sampling event</td><td>Canister conditions must be recorded upon receipt by the laboratory.
If canister pressure is recorded as greater than -25 mmHg, results summary form is not included in the data validation report, electronic data deliverable spreadsheet field “Reportable Y/N” is populated with “N” for the sample, and the situation is described in the validation narrative with the conclusion that the sample results are not reported.
If the canister pressure is recorded less than -10 mmHg, qualify all results estimated “J/UJ”.
If the canister pressure is recorded at zero or at positive pressure, sample data associated with this canister are unusable and qualified “R”.</td></tr>
<tr><td>Analytical sequence</td><td>Recommended for each 24-hour time period</td><td>Perform bromofluorobenzene (BFB) instrument performance check.
Initiate multi-point calibration or daily calibration check.
Analysis of laboratory method blank.
Sequence ends, with analysis of 20 or less samples.
If this is not met, apply professional judgment to samples analyzed outside a valid sequence.</td></tr>
<tr><td>Instrument performance check / BFB Tune</td><td>Demonstrates verification of mass calibration and resolution of GS/MS system</td><td>BFB key ions and ion abundance criteria:

<table><tr><th>Mass</th><th>Ion abundance criteria</th></tr><tr><td>50</td><td>8.0 to 40.0 Percent of m/e 95</td></tr><tr><td>75</td><td>30.0 to 66.0 Percent of m/e 95</td></tr><tr><td>95</td><td>Base peak, 100 Percent Relative Abundance</td></tr><tr><td>96</td><td>5.0 to 9.0 Percent of m/e 95</td></tr><tr><td>173</td><td>Less than 2.0 Percent of m/e 174</td></tr><tr><td>174</td><td>50.0 to 120.0 Percent of m/e 95</td></tr><tr><td>175</td><td>4.0 to 9.0 Percent of m/e 174</td></tr><tr><td>176</td><td>93.0 to 101.0 Percent of m/e 174</td></tr><tr><td>177</td><td>5.0 to 9.0 Percent of m/e 176</td></tr></table>
If these criteria are not met, sample data associated with this instrument tune are unusable and qualified “R”.</td></tr>
</table>

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Issue	Description	DV Approach and Qualifier Actions
Initial Calibration	Demonstrates instrument sensitivity and linearity	• Must be calibrated at five concentrations, one of which should be at the reporting level. • Relative response factor (RRF) percent relative standard deviation (%RSD) for each target analyte must be less than 30%. • Relative retention time (RRT) for each target analyte at each calibration level must be within 0.06 units of the mean RRT. • Internal standard area response at each calibration level must be within 40% of the mean area response over the initial calibration range. • Internal standard retention time shift at each calibration level must be within 20 seconds of the mean retention time over the initial calibration range. If these criteria are not met, positive results are qualified as estimated "J" and non-detects as estimated "UJ". Professional judgment may deem sample data associated with this calibration as unusable and qualified "R" in any case where retention time shifts or sensitivity suggest that positive results could be missed (false negatives).
Daily calibration	Demonstrates the instrument continues to remain under control	• Must be analyzed, using mid-level calibration standard. • RRF for each target analyte must be less than 30% of the mean RRF established in the initial calibration. • Each target analyte concentration in the daily calibration must be within 30% of the true value. If these criteria are not met, positive results are qualified as estimated "J" and non-detects as estimated "UJ". Professional judgment may deem sample data associated with this calibration as unusable and qualified "R" in any case where retention time shifts or sensitivity suggest that positive results could be missed (false negatives).
Blank analyses	Demonstrates no contaminants in the analytical system, and that the instrument continues to remain under control	• Must be analyzed at least once in a 24-hour analytical sequence. • Must be analyzed after the calibration standard(s) and before any sample. • In the event a high concentration sample is encountered, a blank analysis should be performed immediately after the sample is completed to check for carry over effects. • Internal standard area responses in the blank must be within 40% of the mean area responses in the most recent valid calibration. • Internal standard retention times in the blank must be within 0.33 minutes of the most recent valid calibration. For target analytes which have been determined to be contaminants, follow NFG guidance for qualification of sample data. Professional judgment may deem sample data associated with this blank as unusable and qualified "R" in any case where retention time shifts or sensitivity suggest that positive results could be missed (false negatives).

Issue	Description	DV Approach and Qualifier Actions
Sample analysis		• Must be analyzed within 24 hours of calibration standard that meets technical criteria. • Must be analyzed after laboratory method blank that meets technical criteria. • All target analytes must be within calibration range. • Internal standard retention times in the sample must be within 0.33 minutes of the most recent valid calibration. If these criteria are not met, professional judgment may be exercised. Professional judgment may include qualifying data as unusable and qualified "R" in any case where retention time shifts or sensitivity suggest that positive results could be missed (false negatives) or where positive results may be false positives.